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Supporting Information

Millimeter-sized Flat Crystalline Sheet Architectures of Fullerene Assemblies with Anisotropic Photoconductivity

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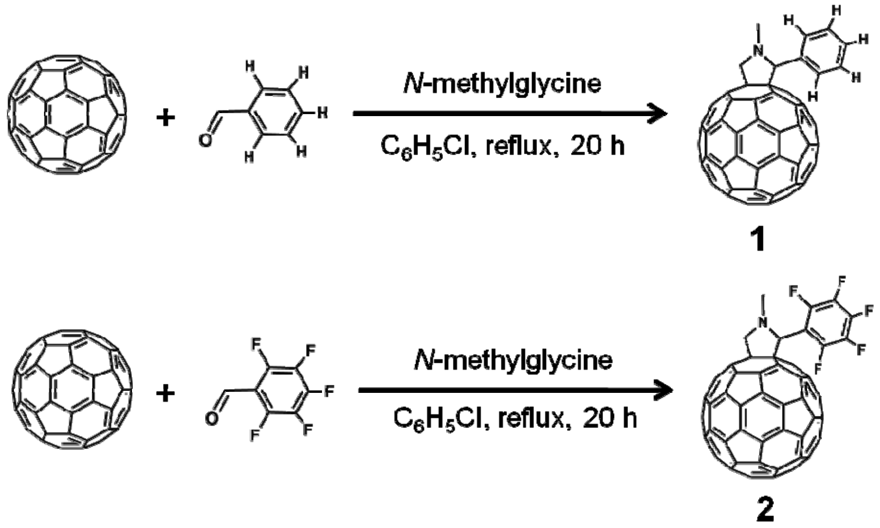
1. Experimental Details

General Procedures: Unless otherwise stated, all starting materials and reagents were purchased from commercial suppliers and used without further purification. ^{1}H (400 MHz) spectra were measured on Bruker DMX400 spectrometer using TMS as internal standard. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were obtained Shimadzu AXIMA-CFR Plus station using 2-(4-hydroxyphenylazo)-benzoic acid (HABA) as the matrix. UV-vis absorption spectra in solution were recorded on Varian Cary50 Conc spectrophotometer. The crystalline objects were directly characterized with Low Field Emission-SEM (SU-8000, Hitachi, 1.0 kV), XRD (Brucker D8 Advance), and AFM (Nanoscope IIIa (Veeco), tapping mode). Optical micrographs were taken using an Olympus BX51 microscope equipped with an MP5Mc/OL digital camera. The flash-photolysis-time-resolved microwave conductivity (TRMC) measurement was carried out using X-band (9 GHz) microwave circuit at low power (approximately 3 mW) and a nanosecond laser irradiation at 355 nm with photon density of 1.8 x 10^{16} cm^{-2}. TRMC samples were prepared by pasting on a quartz plate with double-sticky tape (the tape was confirmed not to disturb any TRMC signal). The obtained transient conductivity ($\Delta\sigma$ in S m^{-1}) was converted to the product of the quantum yield: ϕ and the sum of charge carrier mobilities: $\Sigma\mu$ (= $\mu_+ + \mu_-$), by $\phi\Sigma\mu = \Delta\sigma\,(eI_0F_{\mathrm{light}})^{-1}$, where e, I_0, and F_{Light} are the unit charge of a single electron (in C), incident photon density of excitation laser (in m^{-2}), a correction (or filling) factor (in m^{-1}), respectively. The F_{Light} was calculated by taking into consideration the geometry and optical properties of the sample such as the size, laser cross-section, and absorption of the excitation laser. For the measurement of anisotropic conductivity, a quartz plate was inserted into a microwave resonant cavity parallel or perpendicular to the electric field of the standing wave. The intensity of conductivity signals were calibrated by the control experiment using an isotropic conjugated polymer film. Single crystal analysis was carried out using VariMax with Saturn, using the X-ray source of MoK(α) λ = 0.71075 Å, 50 kV, 24 mA, -180 ^{o}C. Calculations were conducted using density functional theory method at B3LYP/6-31G* level (Spartan 08, Wavefunction Inc., 18401 Von Karman Ave., Suite 370 Irvine, California).

2. Synthesis and characterization

The fullerene C_{60} derivatives **1** and **2** were synthesized as per the reported procedures [S1] as shown in Scheme S1.



Scheme S1: Synthetic scheme of **1** and **2**.

1: A mixture of benzaldehyde (100 mg, 0.942 mmol), C_{60} (1.02 g, 1.413 mmol), and *N*-methylglycine (420 mg, 4.71 mmol) in dry chlorobenzene (400 mL) was refluxed for 20 h. After the reaction mixture was cooled to 20 °C and evaporated, the crude product was filtered through a plug twice ($CHCl_3$). Removal of the solvent in vacuum and the preparative GPC (Bio-beads S-X3, Toluene) followed by column chromatography (silica gel, hexane/$CHCl_3$ 1:1) afforded **1** (410 mg, 51%) as a brown solid. Decomposition temperature ~315 °C; FT-IR (KBr): 2779, 2836, 2944, 3024 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$), $\delta = 2.84$ (*s*, 3H, NC*H*$_3$), 4.30-4.28 (*d*, 1H, CH_2, $J = 9.2$ Hz), 4.96 (*s*, 1H, CH^*), 5.03-5.00 (*d*, $J = 9.2$ Hz, 1H, C*H*$_2$), 7.3 (*m*, 1H, Ar), 7.47 (*m*, 2H, Ar), 7.84 (*m*, 2H, Ar); MALDI-TOF-MS: calcd for $C_{69}H_{11}N$ 853.09; found 853.04 [M^+].

2: A mixture of 2,3,4,5,6-pentafluorobenzaldehyde (200 mg, 1.01 mmol), C_{60} (1.1 g, 1.529 mmol), and *N*-methylglycine (450 mg, 4.53 mmol) in dry chlorobenzene (400 mL) was refluxed for 20 h. After the reaction mixture was cooled to 20 °C and evaporated, the crude product was filtered through a plug twice ($CHCl_3$). Removal of the solvent in vacuum and the preparative GPC (Bio-beads S-X3, Toluene) followed by column chromatography (silica gel, hexane/$CHCl_3$ 1:1) afforded **1** (450 mg, 48%) as a brown solid. Decomposition temperature ~335 °C; FT-IR (KBr): 1650, 2327, 2780, 2845, 2951 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$), $\delta = 2.86$ (*s*, 3H, NC*H*$_3$), 4.22-4.20 (*d*, 1H, CH_2, $J = 9.6$ Hz), 5.04-5.01 (*d*, 1H, C*H*$_2$, $J = 9.6$ Hz,), 5.46 (*s*, 1H, CH^*); ^{19}F NMR (300 MHz, $CDCl_3$), $\delta = -137.1$ (*d*, 1F), -143.2 (*m*, 1F), -155.1 (*t*, 1F), -162.8 (*m*, 1F), -163.8 (*m*, 1F); MALDI-TOF-MS: calcd for $C_{69}H_6F_5N$ 943.04; found 942.98 [M^+].

3. Supporting Information Figures

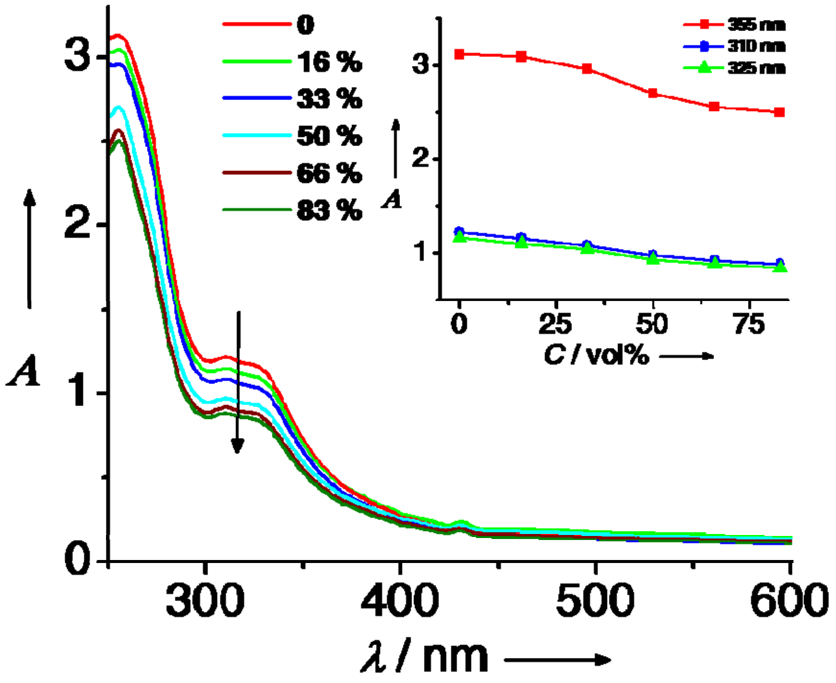


Figure S1. a) Absorption spectra of the coassembly of **1** and **2** (1:1) in chloroform (1 x 10^{-5} M) upon addition of increasing vol% of *n*-hexane ($l = 1$ cm); inset shows the corresponding variation of the absorbance at different wavelengths.

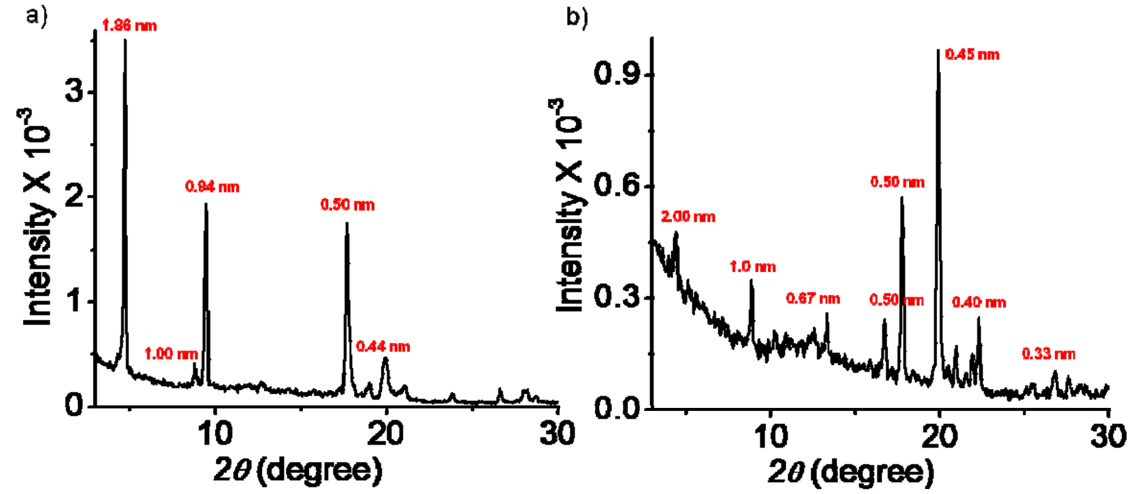


Figure S2. XRD profiles of crystalline sheets of a) **1** and b) **2**.

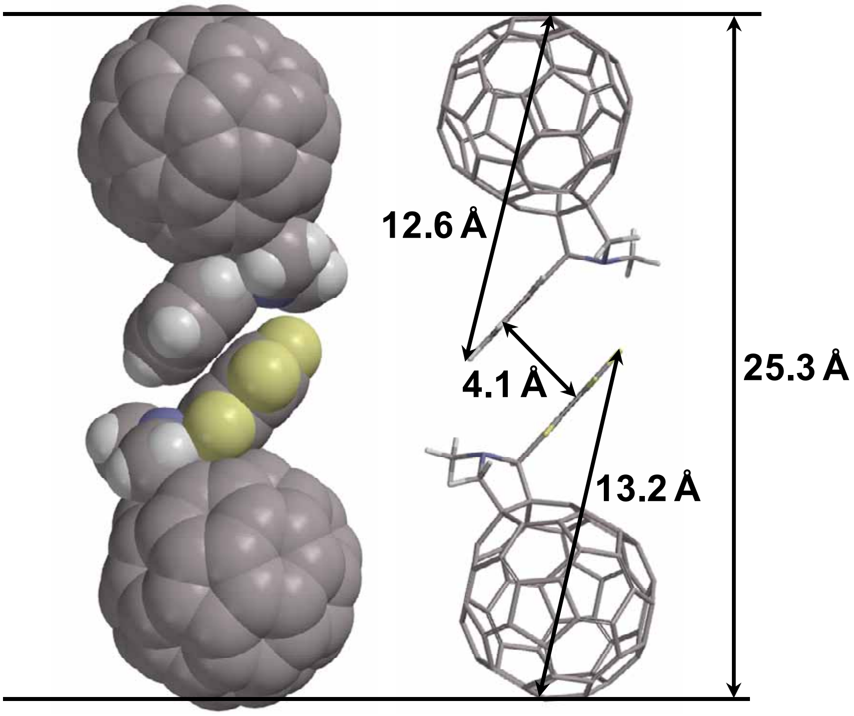


Figure S3. The bimolecular length assumed using optimised molecular structures of **1** and **2** by B3LYP/6-31G* level density functional theory (DFT) calculation.

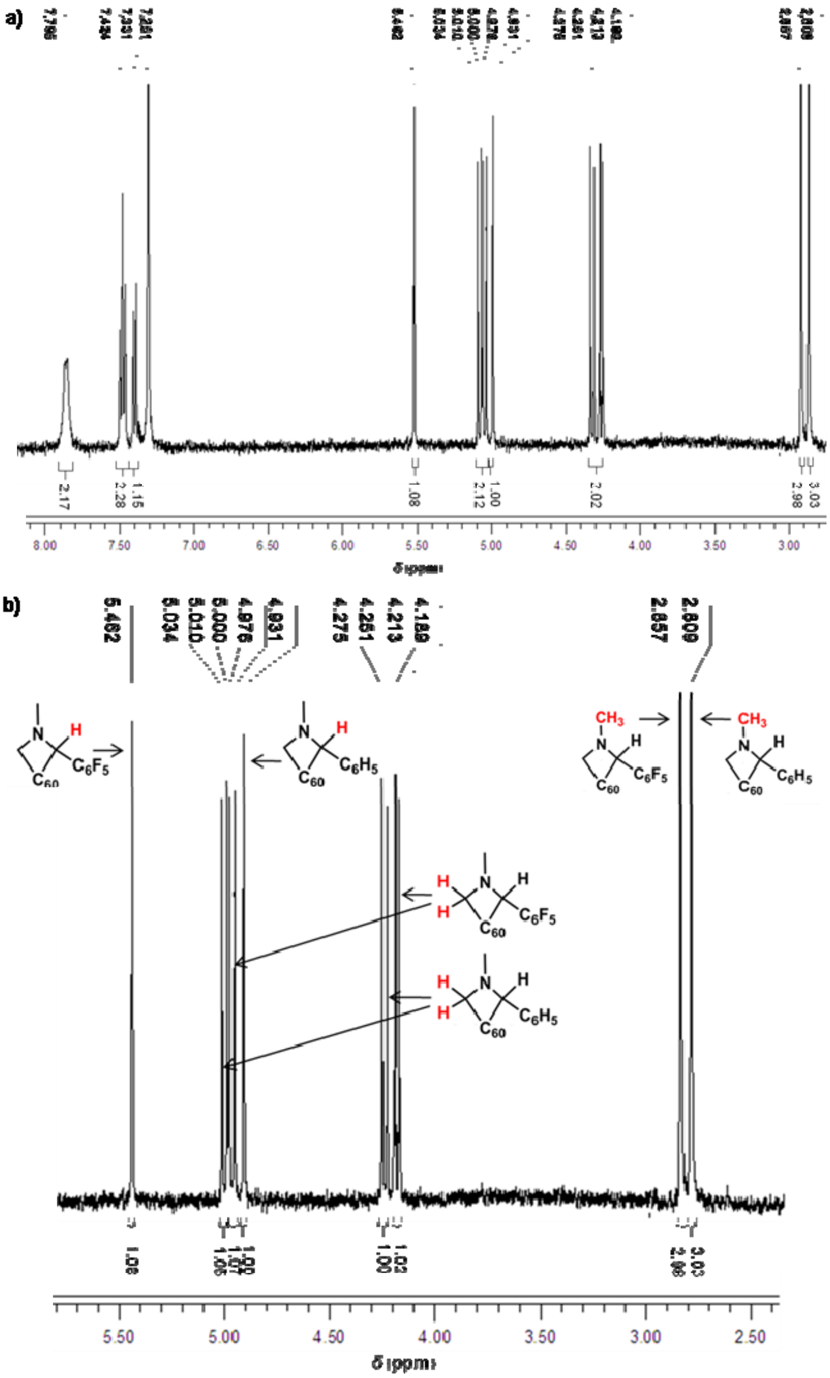


Figure S4. a) ^{1}H NMR spectrum of the coassembly of **1** and **2** in $CDCl_3$, b) zoomed spectrum showing the 1:1 complexation in the solution.

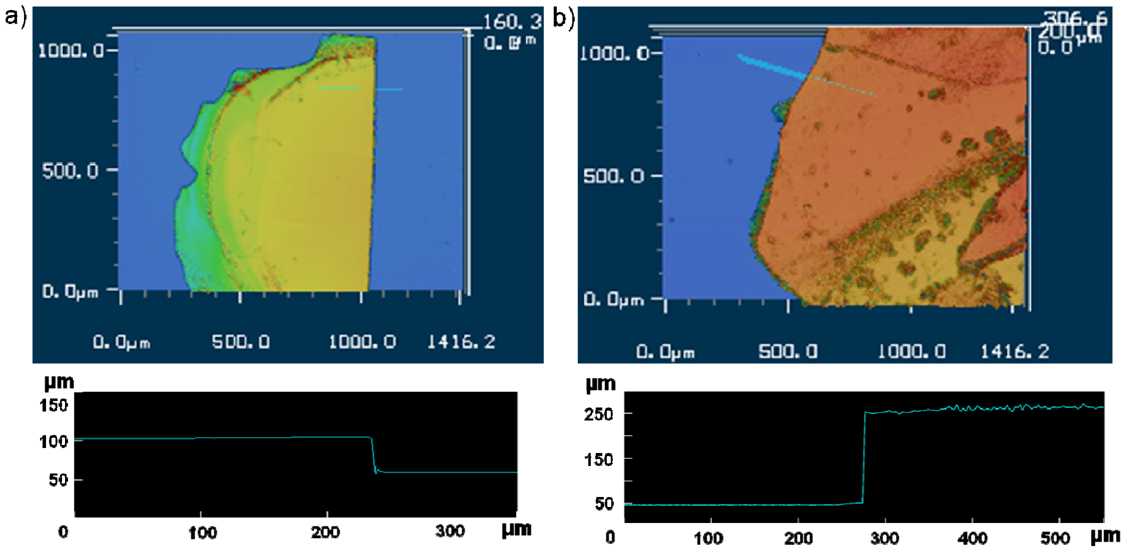


Figure S5. 3D-LSM images of the coassembled crystalline sheets of **1** and **2** (1:1). The thinner (a) and thicker (b) sheets have ~50 and ~200 μm thickness, respectively.

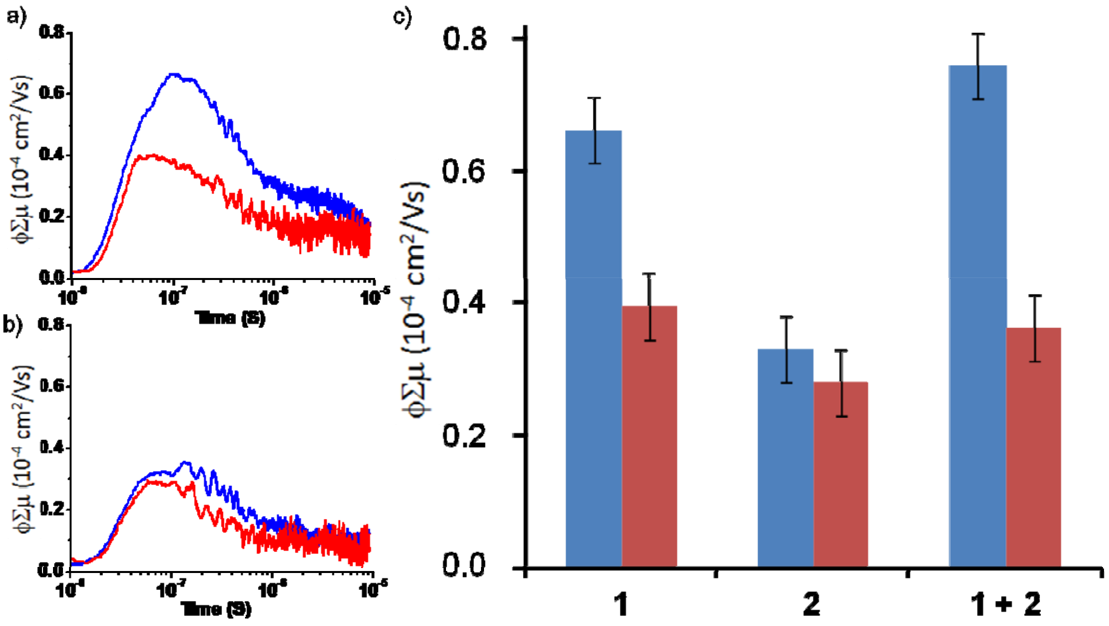


Figure S6. TRMC transient decay profiles in the parallel (—) and perpendicular (—) directions of a) **1** and b) **2** under an excitation at λ = 355 nm by 1.8 x 10^{16} photons cm^{-2} pulse^{-1}. c) Comparison of the charge carrier mobilities of the crystals of **1**, **2** as well as **1** and **2** in the parallel (left) and perpendicular (right) directions.

Photoconductivity value of 0.66 x 10^{-4} cm^2/Vs in parallel and 0.33 x 10^{-4} cm^2/Vs in perpendicular directions with anisotropy of 1.7 was obtained for **1** due to better organisation in the crystalline assembly. It has been evidenced in the XRD result that the presence of fluorine atoms hinders the smooth ordering of **2** in the sheets and thereby lowered the photoconductivity value to 0.33 x 10^{-4} cm^2/Vs in parallel and 0.28 x 10^{-4} cm^2/Vs in perpendicular directions with an anisotropy factor of 1.2. The coassembled sheets of **1** and **2** exhibited 0.76 x 10^{-4} cm^2/Vs in parallel and 0.36 x 10^{-4} cm^2/Vs in perpendicular directions with an anisotropy factor of 2.1, which is the best anisotropic feature among crystals studied here.

Reference

[S1] M. Maggini, G. Scorrano, M. Prato, *J. Am. Chem. Soc*. 1993, **115**, 9798.